ORGANIC
LETTERS

2001
Vol. 3, No. 2
169−171

Synthesis of Configurationally Defined Sexi- and Octinaphthalene Derivatives

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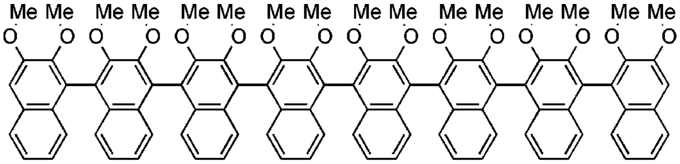
Received November 9, 2000

ABSTRACT



(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-isomer
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-isomer
(*S*,*S*,*S*,*S*,*S*,*R*,*S*)-isomer

Configurationally defined optically active octinaphthalenes were synthesized using the oxidative coupling of optically active quaternaphthalenes with a 2-hydroxynaphthol moiety as a key reaction. The absolute configuration was determined by comparison with products of [6 + 2] coupling.

Monodisperse π-conjugated oligomers have recently attracted attention due to their potential application in material sciences.[1] Oligo(*p*-phenylene)s have received special attention and have been used as backbones for artificial proton channels[2] and β-barrels[3] and as rigid spacer units in an artificial receptor of cyclic dipeptides.[4] Oligo(*p*-phenylene)s are also important model compounds for poly(*p*-phenylene)s, since some poly(*p*-phenylene)s are remarkable organic conductors upon doping[5] and are also used as laser materials.[6] The rod can contain 15[7] or even 16[8] phenyl rings. On the other hand, little attention has been paid to rod-shaped oligonaphthalenes connected at the 1,4-positions. The longest monodisperse oligonaphthalene is a sexinaphthalene.[9,10] It has been reported that a stereochemically defined quaternaphthalene shows characteristics of an organic zeolite.[11] It would be interesting to determine whether higher oligonaphthalenes also show such characteristics. We report here the synthesis of optically active sexi- and octinaphthalenes.

The synthesis of sexinaphthalenes started from the optically active ternaphthalene **1**[12] (Scheme 1). Methylation of (*S*,*S*)-**1** afforded (*S*,*S*)-**2**, which was converted into monohydroxy ternaphthyl (*S*,*S*)-**3** by hydrogenolysis, in 82% overall yield. Oxidative coupling[13] of **3** afforded sexinaphthalenes **4** and **8** in respective yields of 31% and 38%. The

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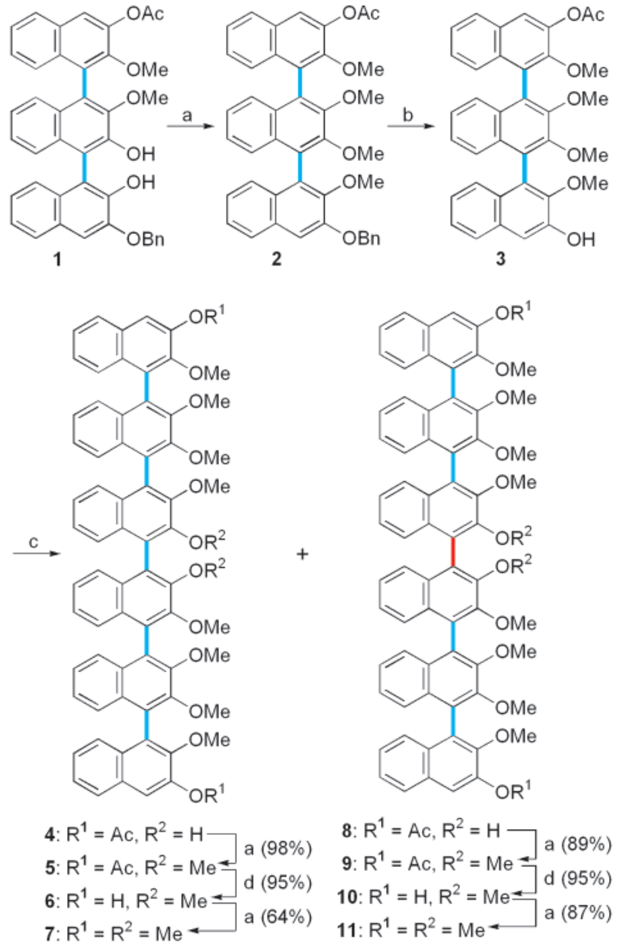
10.1021/ol006843c CCC: $20.00

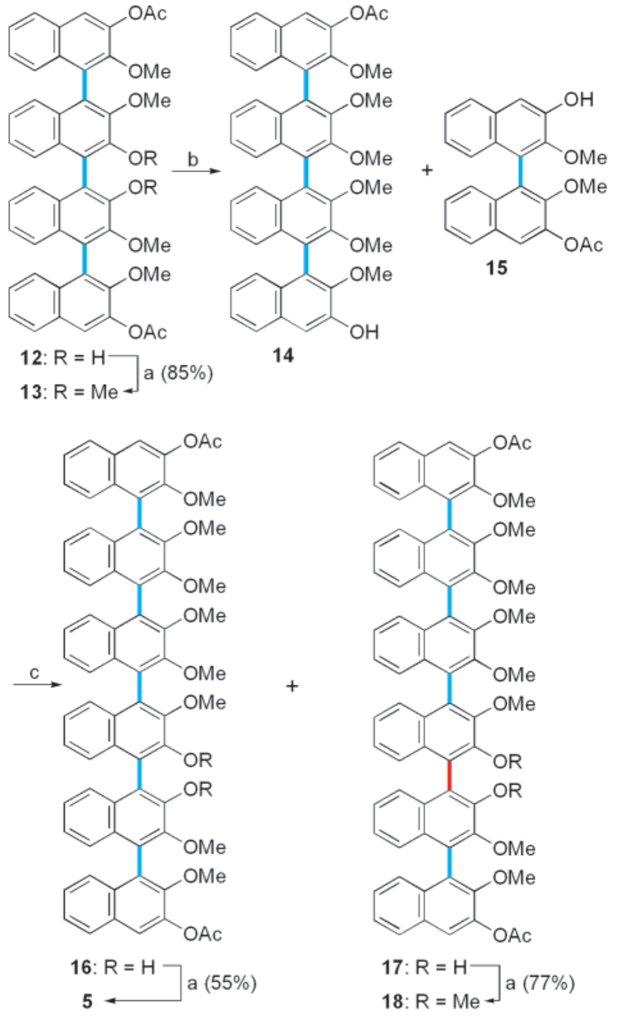
Scheme 1. The [3 + 3] Construction of Sexinaphthalene



only difference between **4** and **8** is the absolute stereochemistry of the newly created bond, which was unambiguously determined by synthesis via another route that included the [4 + 2] construction of sexinaphthalenes (Scheme 2). The known quaternaphthalene **12**[12] was methylated to give **13**, partial hydrolysis of which afforded **14** in 40% yield. The oxidative coupling of **14** and **15** afforded sexinaphthalenes **16** and **17** in respective yields of 18% and 16%, along with **12** and its isomer with an *R*-configuration at the central bond.[14] Methylation of **16** gave **5**, which is identical to one of the products of the homocoupling of **3**, while methylation of **17** gave **18**, which is distinct from both **5** and **9**. These findings clearly support the absolute configurations of the coupling products **4**, **8**, **16**, and **17**.

A similar strategy was used to synthesize octinaphthalenes and to determine their absolute stereochemistry (Scheme 3). Oxidative coupling of quaternaphthalene **14** gave **19** (14%) and **23** (18%). Methylation of **19** followed by hydrolysis gave **21**. Treatment of **21** with CH_3I/K_2CO_3 in acetone converted **21** into **22**, which has a methoxy group as a uniform substituent. The diastereomer **23** was transformed to **26** through the same sequence of reactions as those for **19**. The [6 + 2] construction of octinaphthalenes is also shown in Scheme 3. Partial hydrolysis of **5** gave **27**, which was then oxidatively coupled with **15** to give **28** (13%) and **29** (22%). Methylation of **28** gave **20**, while that of **29** gave **30**, which determined the absolute configuration of the products **28** and **29** as shown in Scheme 3.

Scheme 2. The [4 + 2] Construction of Sexinaphthalene



Another interesting aspect of oligonaphthalenes is their molecular shape, which is reminiscent of the banisters of a spiral staircase, and their π-system, which is totally different from that of helicenes.[15] An interesting question is how many naphthyl rings are required to complete a full turn of the helix. An X-ray crystal structural analysis of a quaternaphthalene revealed that four naphthyl units are insufficient.[12] Since none of the sexi- or octinaphthalenes gave crystals

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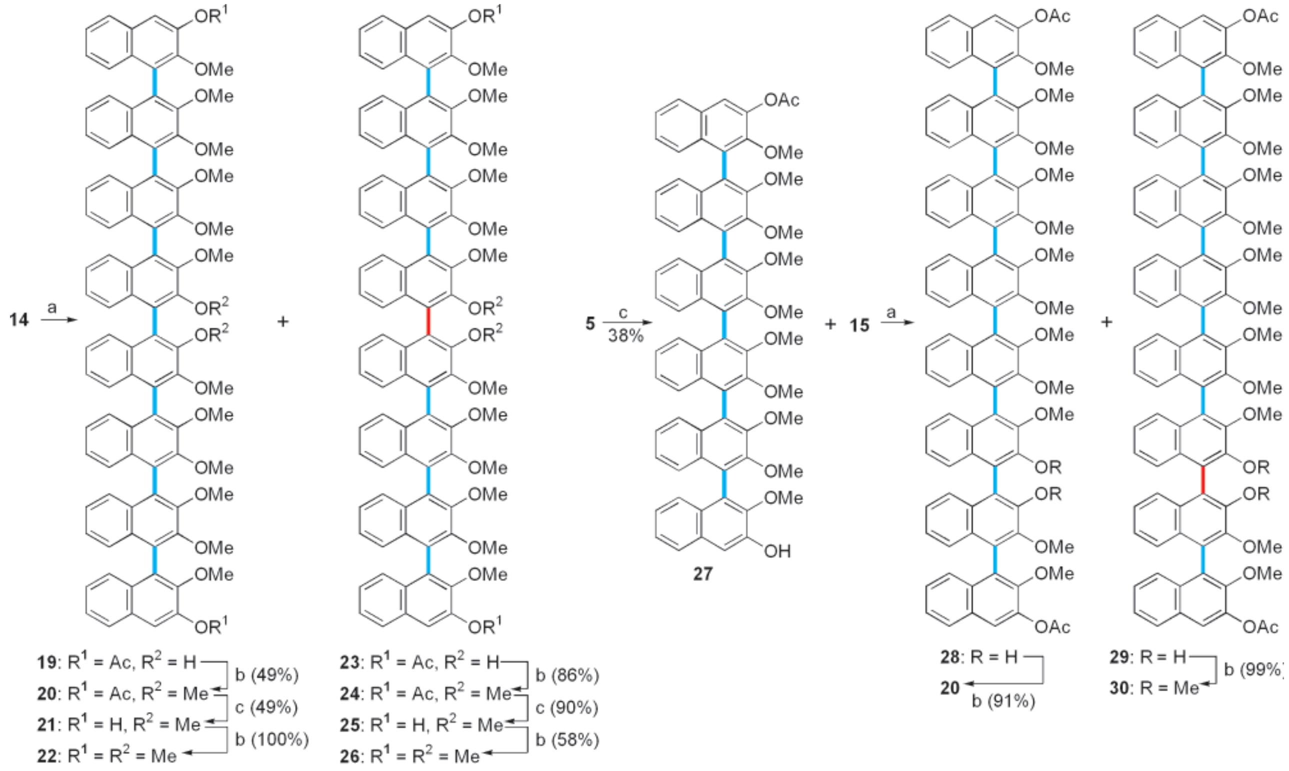
[14] To save more valuable quaternaphthalene **14**, a large excess of **15** was used. Thus, a solution of **14** (96 mg, 0.13 mmol) and **15** (252 mg, 0.65 mmol) in CH_2Cl_2(12 mL) was added into a mixture of $CuCl_2$ (210 mg, 16 mmol) and α-phenylethylamine (0.25 mL, 2.0 mmol) in MeOH (0.6 mL) and the mixture was stirred for 27 h at room temperature under N_2. After addition of 2 N HCl to decompose the copper−amine complex the mixture was condensed under reduced pressure. Extractive workup followed by preparative TLC gave **16** (27 mg), **17** (24 mg), **12** (66 mg), and its isomer with *S*,*R*,*S*-configuration (51 mg).

[15] This type of helix was called a Geländer-type molecule. See: Kiupel, B.; Niederalt, C.; Nieger, M.; Grimme, S.; Vögtle, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3031−3034.

Scheme 3. Synthesis of Octinaphthalenes



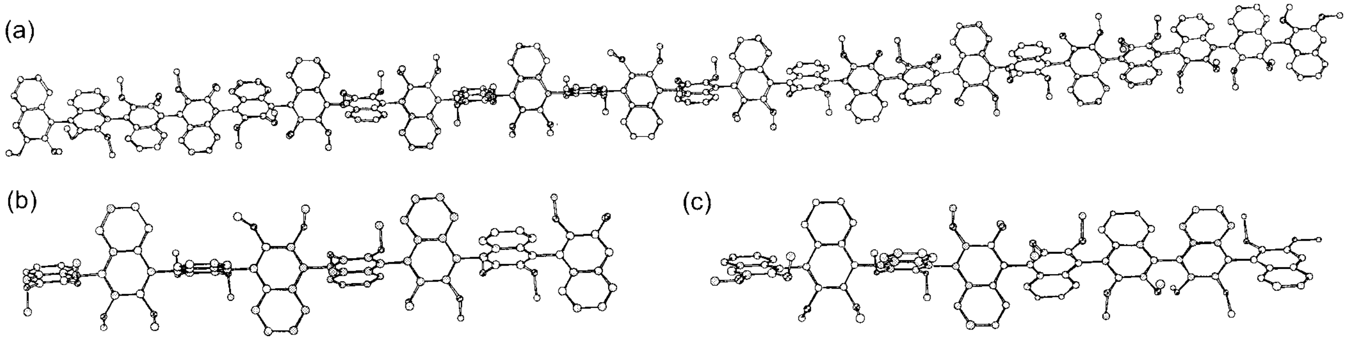


Figure 1. (a) The most stable conformation of the 24-mer calculated by MacroModel (version 6.0). (b) The central eight naphthalenes of the 24-mer. (c) The most stable conformation of octinaphthalene **22** calculated by MacroModel (version 6.0).

suitable for X-ray analysis, the most stable conformation of **22** was calculated by MacroModel/MM2 (version 6.0). The results indicated that five to six naphthyls are necessary for a turn (Figure 1c). The calculation for the corresponding 24-mer revealed that the helix repeated a full turn every five to six naphthyls (Figure 1a). The central eight naphthalene units of the 24-mer were extracted and compared with octinaphthalene **22** (Figure 1b and 1c). While the two conformations are quite similar, a slight lag was observed for a turn.

The use of optically active sexi- and octinaphthalenes for new materials and for molecular recognition is currently under investigation.

Supporting Information Available: Experimental procedures for compounds **4**, **8**, **28**, and **29** and characterization of **4**, **7**, **8**, **11**, **16**, **17**, **19**, **22**, **23**, **26**, **28**, and **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL006843C